

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

**Applicant(s):** Klingenberg et al.  
**Serial No.:** 10/715,916                      **Group Art Unit:** 1711  
**Filed:** 18 November 2003                      **Examiner:** R. Sergent  
**Atty. Docket No.:** 06471 USA                      **Confirmation No.:** 6531  
**For:** AQUEOUS POLYURETHANE DISPERSION AND METHOD FOR MAKING  
AND USING SAME

**DECLARATION PURSUANT TO 37 C.F.R. § 1.132**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Eric Howard Klingenberg, Ph.D., a citizen of the United States hereby declare and state:

1. I have a Bachelor's of Science in Chemistry from Geneva College located in Beaver Falls, PA and a Ph.D. in Chemistry from The Pennsylvania State University located in State College, PA.

2. I am currently employed by Air Products and Chemicals, Inc. ("APCI"), the assignee of the present patent application. I have been employed by APCI for approximately 5 years. My present position is Manager of the Specialty Polymer Group. In this capacity I lead a team of researchers and engineers in the development of new polymeric materials and processes for advanced applications including microelectronic device manufacturing.

3. I am a co-inventor on the present application, U.S. patent application Serial No. 10/715,916 ("the 916 application"), along with Shafiq Fazel.

4. I have reviewed the 916 application, which I understand to have been filed in the United States Patent & Trademark Office on November 18, 2003, as well as copies of the Final

Office Action dated March 19, 2007 ("the Final Action"). I have also reviewed the references cited in this correspondence, namely, U.S. patent application Publication No. US 2003/0083457 to Schafheutle et al. ("Schafheutle"), U.S. Patent No. 6,515,070 to Kobylanska et al. ("Kobylanska"), U.S. Patent No. 5,354,807 to Dochniak et al. ("Dochniak"), U.S. Patent No. 5,270,433 to Klauck et al. ("Klauck"), U.S. Patent No. 5,576,382 to Seneker et al. ("Seneker"), and U.S. Patent No. 4,855,077 to Shikinami et al. ("Shikinami"). I have also reviewed the Reply to which this declaration is attached.

5. I understand that the independent claims in the 916 application, *i.e.*, Claims 15, 16, 17, 22, 23, and 25, have been amended, in part, as follows:

- (a) the "chain extending agent comprising an organic diamine" was amended to recite that the diamine is selected from the group consisting of:  
ethylene diamine, 1,6-hexamethylene diamine, and 1,5-diamino-1-methylpentane;
- (b) the particle size of the polyurethane polymer molecules in the aqueous dispersion is recited as "less than about 2 microns";
- (c) the polyurethane polymer is specified to be non-crystalline; and
- (d) it is specified that the steps of the claimed methods (independent Claims 15, 16, 22, 23 and 25) are "conducted sequentially".

6. In view of these amendments, I understand that independent Claim 1, for example, now defines a process for forming an aqueous polyurethane dispersion, the process comprising: **(1)** providing an isocyanate terminated prepolymer by reacting (i) at least one diisocyanate comprising about 50% by weight or greater of  $\alpha,\alpha,\alpha,\alpha$ -tetramethylxylene diisocyanate, (ii) at least one difunctional polyol comprising poly(propylene oxide) diol, and (iii) at least one isocyanate reactive compound comprising an acid functional group and at least two isocyanate reactive groups selected from the group consisting of a hydroxy, a primary amino, a secondary amino, and combinations thereof; **(2)** neutralizing the isocyanate reactive compound (iii) with a

neutralizing agent comprising an amine group; **(3)** reacting the isocyanate terminated prepolymer with at least one chain terminating agent; **(4)** dispersing the isocyanate terminated prepolymer in water; and **(5)** reacting the isocyanate terminated prepolymer with at least one chain extending agent comprising an organic diamine selected from the group consisting of: ethylene diamine, 1,6-hexamethylene diamine, and 1,5-diamino-1-methyl-pentane, wherein the polyurethane polymer has a weight average molecular weight ranging from 40,000 to 60,000 g/mol, wherein the particle size of the polyurethane polymer molecules in the aqueous dispersion is less than about 2 microns, wherein the polyurethane polymer is non-crystalline, and wherein the aforementioned steps are conducted sequentially.

7. I understand from the Final Action that the Patent Office asserts that the claims of the 916 application are unpatentable because the differences between the claimed invention and the cited references are such that the claimed invention would have been obvious at the time that the methods were invented to a person having ordinary skill in the field to which the claimed invention pertains.

8. I do not agree with the Patent Office that the differences between the claimed invention and the cited references are such that the claimed invention would have been obvious at the time that the invention was made to a person having ordinary skill in the field to which the claimed invention pertains. In this regard, the cited references – either alone or in combination do not teach or suggest an aqueous polyurethane dispersion as defined by the claims of the 916 application nor do they teach or suggest the specific method for making the claimed dispersions, which have a unique set of properties that make them useful as adhesives for electrical components.

9. In particular, the following experimental data will conclusively demonstrate that the recited order of addition, particle size, molecular weight range, and non-crystalline nature of the polyurethane dispersions of the present invention directly translate into surprising and unexpected results relative to that disclosed by the prior art.

Order of Addition & Particle Size

10. The invention of the 916 application provides a composition and a method for preparing a polyurethane dispersions with specific properties related to the uniform coating of the wet dispersion, exemplary lamination of the dry adhesive film to substrates that have some relief structure such as those substrates common in electronic devices, while maintaining the desired adhesive performance necessary for proper device operation. Specifically, the adhesive prepared as described in the invention has a uniform particle size less than 2 microns. The particle size of these dispersions is very important given the small feature size in sophisticated devices such as those used in electronics. Large particles, *i.e.*, those greater than 2 microns, which may exist in dispersions prepared by a prior art process, can potentially lead to defects that cause improper working of the device. These defects are characterized by the existence of electrical shorts or visual defects in the case of display applications. In displays these defects are usually areas in which the device does not display an appropriate image because of the improper electrical contact caused by the existence of large particles.

11. I understand that the examiner alleges that claims 1-4, 6-17, 19, and 21-25 are rejected as being unpatentable over Schafheutle in view of Kobylanska, Dochniak, Klauck, and Seneker. These references teach that there is latitude with respect to the sequence of neutralization, chain termination, dispersion, and chain extension and it is the examiners position that the instantly claimed sequence in 916 would have been obvious to one of ordinary skill in the art.

12. I respectfully disagree with the examiners assertion that the claimed sequence would have been obvious to one of ordinary skill in the art. Specifically, Schafheutle makes no mention of particle size and, at paragraph [0049] teaches that there is latitude with respect to neutralization and dispersion. Seneker, at column 7, line 30, likewise teaches that there is latitude with respect to the neutralization and dispersion process. Kobylanska, at column 4, line

55, mentions that it is preferred to perform the neutralization with the dispersion (*i.e.*, addition of the prepolymer to an aqueous base solution to perform the neutralization and dispersion simultaneously). Dochniak at column 10, line 50, and Klauck, at column 11, line 5, teach the use of an aqueous dispersing medium (*i.e.*, water and base) and that there is latitude with respect to adding the aqueous dispersing medium to the prepolymer or the prepolymer to the aqueous dispersing medium. Therefore, one would not have expected the observed difference in particle size for the dispersion depending on the sequence of addition as we have shown.

13. For example, Exhibit A attached to this declaration provides particle size data obtained using a Horiba particle size analyzer that was collected under my direction indicating that the sequence of neutralization and dispersion do in fact influence the particle size of the polymer in the dispersion. Example B represents the prior teachings such as those found in Schafheutle, Kobylanska, Dochniak, Klauck and Seneker where neutralization and dispersion are carried out ***simultaneously*** through the addition of the prepolymer to an aqueous solution containing a base, triethyl amine, capable of salt formation with an acid such as a carboxylate group. Example A represents the preferred sequence of addition according to the present invention where the prepolymer is neutralized with the base prior to dispersion in water. As evidenced from the particle size data the latter sequence provides a dispersion that has a more uniform particle size distribution and all particles are < 2 microns. Using the methods previously taught in the cited references, the dispersion consists of particles with a non-uniform distribution in size and a substantial fraction of the particles with sizes that exceed 2 microns. Accordingly, in view of the teachings of the prior art, one would not have expected the observed difference in particle size for the dispersion as being dependant on the sequence of addition as we have shown.

Molecular Weight Range

14. The invention of the 916 application provides a composition and a method of production for preparing polyurethane dispersions with specific properties related to the uniform coating of the wet dispersion, exemplary lamination of the dry adhesive film to substrates that have some relief structure such as those in electronic devices, while maintaining adequate adhesive performance. Specifically, this invention claims a polymeric dispersion where the weight average molecular weight (Mw) of the polymer component as measured by Gel Permeation Chromatography (GPC) is from 40,000 g/mol to 60,000 g/mole. The combination of molecular weight and the other claimed characteristics of the polymer provide for a unique balance between lamination properties of the dry adhesive films prepared by coating the dispersion on a substrate and bond strength of the adhesive once the dry adhesive film is laminated to a second substrate.

15. I understand that the examiner alleges that claims 1-4, 6-17, 19, and 21-25 are unpatentable with respect to the claimed molecular weight range given that Schafheutle teaches that materials with a weight average molecular weight greater than 40,000 g/mol are preferred.

16. I understand that, although Schafheutle discloses a preferred weight average molecular weight (Mw) greater than 40,000 g/mole, Schafheutle is completely silent with respect to an upper molecular weight limit or boundary.

17. I understand that Schafheutle discloses a minimum Mw. Specifically, Schafheutle discloses a preferred Mw of >20,000 g/mol in the abstract, while citing a preferred MW of >50,000 g/mole in paragraph [0011], and further discloses preferred examples where the Mw is >40,000 g/mole. Therefore, it is unclear given this disclosure as to the exact minimum MW taught by Schafheutle.

18. In general, lamination quality is assessed through the ability of the adhesive under a given pressure and temperature to make intimate contact with the substrate, including substrates with a specific surface roughness or features (such as those typical in electronic

devices due to wire bond lines) without leaving voids (spaces where the adhesive does not contact the substrate). Because most electronic devices require good connection between conductors to enable proper operation, it is undesirable to have the insulating air gap between these substrates. It is also undesirable to use excessive pressure or temperature to enable the adhesive to flow well enough to provide adequate contact as the application of such extremes often results in damage to the electronic components. The lamination quality for these types of materials is related to the tack and cross-over temperature for the material. The cross over temperature is defined as the temperature at which the loss or liquid like modulus is dominant over the storage or elastic modulus of the material.

19. The bond strength, or adhesive strength, of an adhesive is related to the material's ability to bind to the substrates surface, adhesive strength, and the material's ability to be separated from its own cohesive forces (cohesive strength). The adhesive strength is mainly controlled by the composition of the adhesive with relation to the substrate, while the cohesive strength is related to composition and the number of chain entanglements or Mw.

20. While bond strength and lamination quality are related to the Mw of the polymeric material. The unique molecular weight range that provides adequate lamination quality and bond strength is not known or discussed in the prior art.

21. I respectfully disagree with the Examiner's allegation that the claimed weight average molecular weight (Mw) range would have been obvious in view of Schafheutle because Schafheutle does not teach or suggest an upper limit with respect to the molecular weight. Indeed, we have shown that it is possible to have a material where the Mw is too high and, thus, has unacceptable lamination or adhesion qualities.

22. For example, Exhibit B attached to this declaration provides data that was collected under my direction that reveals the crossover temperature as a function of molecular weight. All materials were made using the claimed process with Example C being representative of a material with an Mw of 30,000 g/mole, Example D being representative of a material with an Mw

of 50,000 g/mol, and Example E being representative of a material with an Mw of 90,000 g/mol. It is clear from this data that Example D has a cross-over temperature intermediate between that of Examples C and E.

23. Exhibit C attached to this declaration provides data that was collected under my direction that reveals the effect of molecular weight on lamination quality. The picture in Exhibit C is that of a frosted glass slide (Fisher Scientific Catalog number 12-544-5CY) that has been in contact with the adhesive film samples of various weight average molecular weights (Mw) at 50°C under a 1.5 kg weight for 1 hour. The adhesive films were prepared by directly coating the wet dispersion on PET release liner at a weight sufficient to give 4 mil dry thickness. The films were air dried for 12 hrs and then dried for 1 hour at 80°C under a nitrogen flow. The description of the samples is as follows: Sample E is a picture of the glass slide with no coating, Sample F used the 35,000 Mw adhesive, Sample G used the 45,000 Mw adhesive, Sample H is with the 50,000 Mw adhesive, Sample I is with the 55,000 Mw adhesive, Sample J is with the 68,000 Mw adhesive, and Sample K is with the 92,000 Mw adhesive. It is clearly seen that the "white" appearance of the slides is where the adhesive did not make good contact with the glass slide, these areas are voids. For samples F through I there is adequate contact with minimal voids. However, Sample J, the 68,000 Mw sample, has large areas near the center of the slide that have very poor contact with the glass slide. This indicates the upper limit of the Mw is near 60,000 Mw for adequate lamination properties.

24. Exhibit D attached to this declaration provides data that was collected under my direction that measures the maximum peel strength for the adhesives as a function of Mw. Peel strength was measured according to the specification described in the 916 application and the data was normalized to the 50,000 g/mole material. This data indicates that the max peel strength is low for materials below 40,000 g/mole and increases with Mw prior to decreasing again after 68,000 g/mole. This clearly indicates that there is a preferred molecular weight range for this material where the adhesive strength is greatest.



25. From the above examples in Exhibits C and D it is conclusive that there is a desired weight average molecular weight range of 40,000 to 60,000 g/mol for the adhesive that gives the best combination of lamination quality and adhesive strength. This range was not obvious in view of the applied prior art.

#### Non-Crystalline Polymers

26. The use of non-crystalline polymers as adhesives in devices where the ionic conductivity of the adhesive material is necessary for proper device operation is critical to maintaining consistent device performance as a function of environmental cycling. Because the degree of crystallinity is affected in polymers by the temperature of the crystalline melt and the rate of cooling, exposure of these types of polymers to different environmental conditions, *i.e.*, temperature and humidity, can bring about changes in the degree of crystallinity of the polymeric material. For ionically conductive polymers, it is only the amorphous regions of the polymer film that contribute to ionic conductivity, not the crystalline regions. Therefore, polymers that crystallize and can undergo changes in crystallinity upon environmental cycling negatively affect the ionic conductivity of the polymer and thus device performance. Therefore, it is preferable to have polymeric adhesives that are free of crystallinity as measured by Differential Scanning Calorimetry (DSC).

27. I understand that the examiner suggest that the use of poly(propylene oxide) diol would be obvious to one skilled in the art to obtain a polyurethane material that would be amorphous or non-crystalline, given the teachings of Szycher at page 3-27, Szycher's Handbook of Polyurethanes, by Michael Szycher, Ph.D. Published by CRC press Boca Raton Florida, copyright 1999.

28. I disagree with the Examiners allegation that the use of poly(propylene oxide)diol as a component in the manufacture of a polyurethane would be expected to provide a polyurethane that is non-crystalline. As stated in the specification, it is possible to use mixtures of polyols that

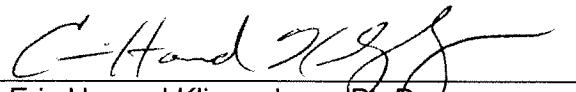
include poly(propylene oxide)diol as one of the polyol components. The use of other polyols may impart crystallinity to the polyurethane.

29. For example, Exhibit E attached to this declaration provides DSC data that was collected under my direction on polymers that were made using the claimed process described in the specification of the present 916 application using TMXDI as the isocyanate but where the polyol component is made up of poly(propylene oxide) diol and another polyol. Example Q is a polyurethane that was made where the polyol component of the polyurethane is made up of 25% hexane diol adipate and 75% poly(propylene oxide)diol by weight. Example R is a polyurethane that was made where the polyol component of the polyurethane is made up of 25% of neopentyl glycol adipate and 75% poly(propylene oxide) diol by weight. In each case the DSC analysis clearly indicates the presence of a heat of fusion peak from the melting of crystalline regions in each Example Q and R. Therefore, it is possible to have polyurethanes with substantial crystallinity even though a significant fraction of the molecule is made up of poly(propylene oxide)diol.

30. Thus, there are significant differences between the inventions defined by the above-identified independent claims and the teachings of the cited references whether each reference is considered alone or in combination with the others.

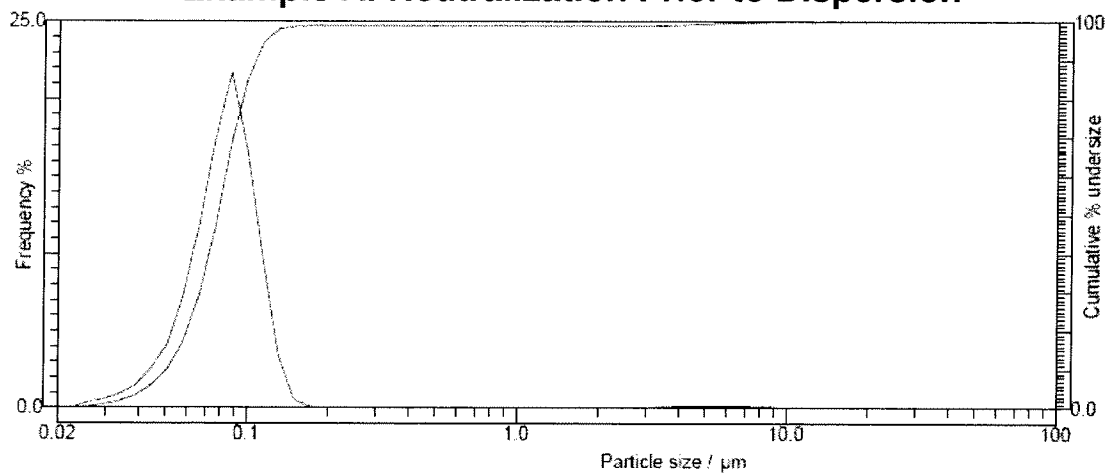
31. I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date: 7/24/2007

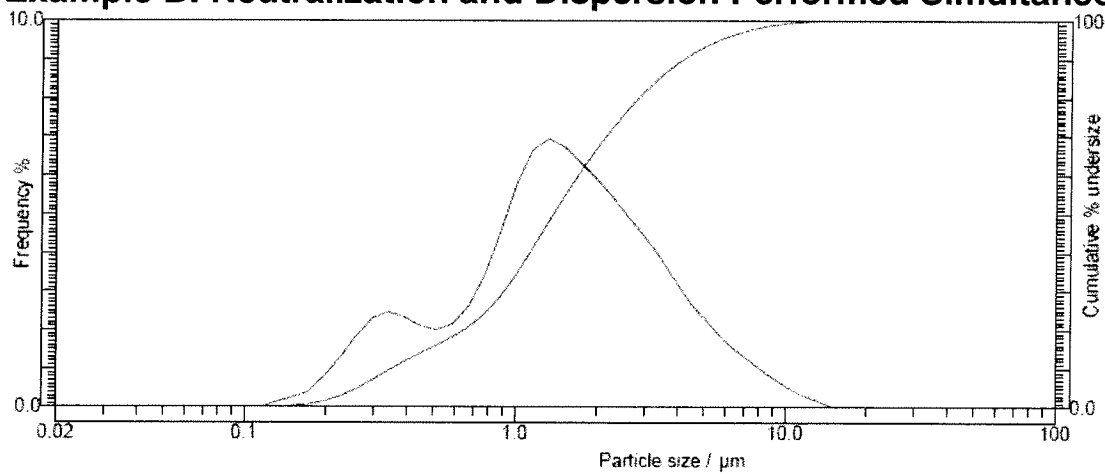
  
Eric Howard Klingenberg, Ph.D.

## EXHIBIT A

**Example A: Neutralization Prior to Dispersion**

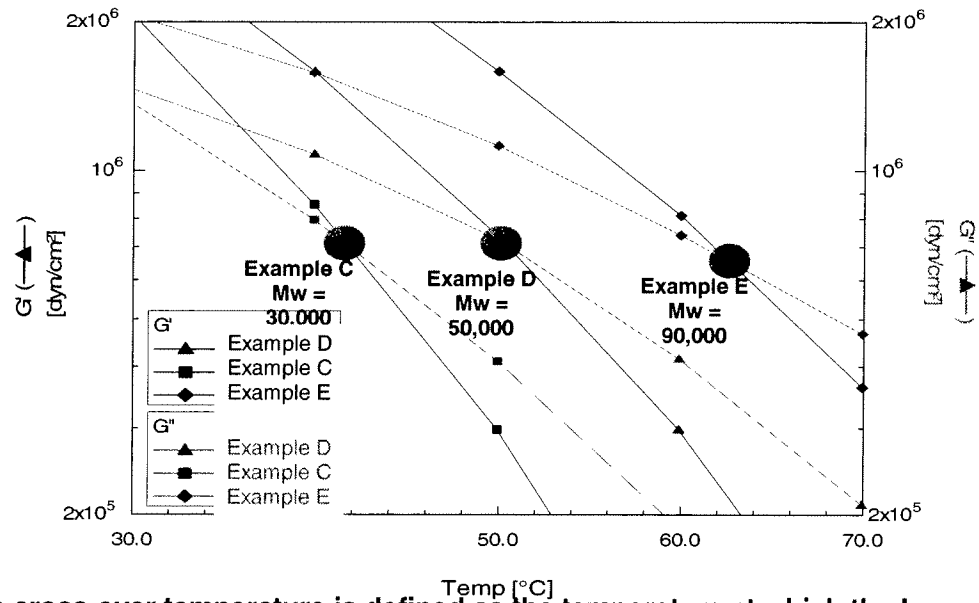


**Example B: Neutralization and Dispersion Performed Simultaneously**



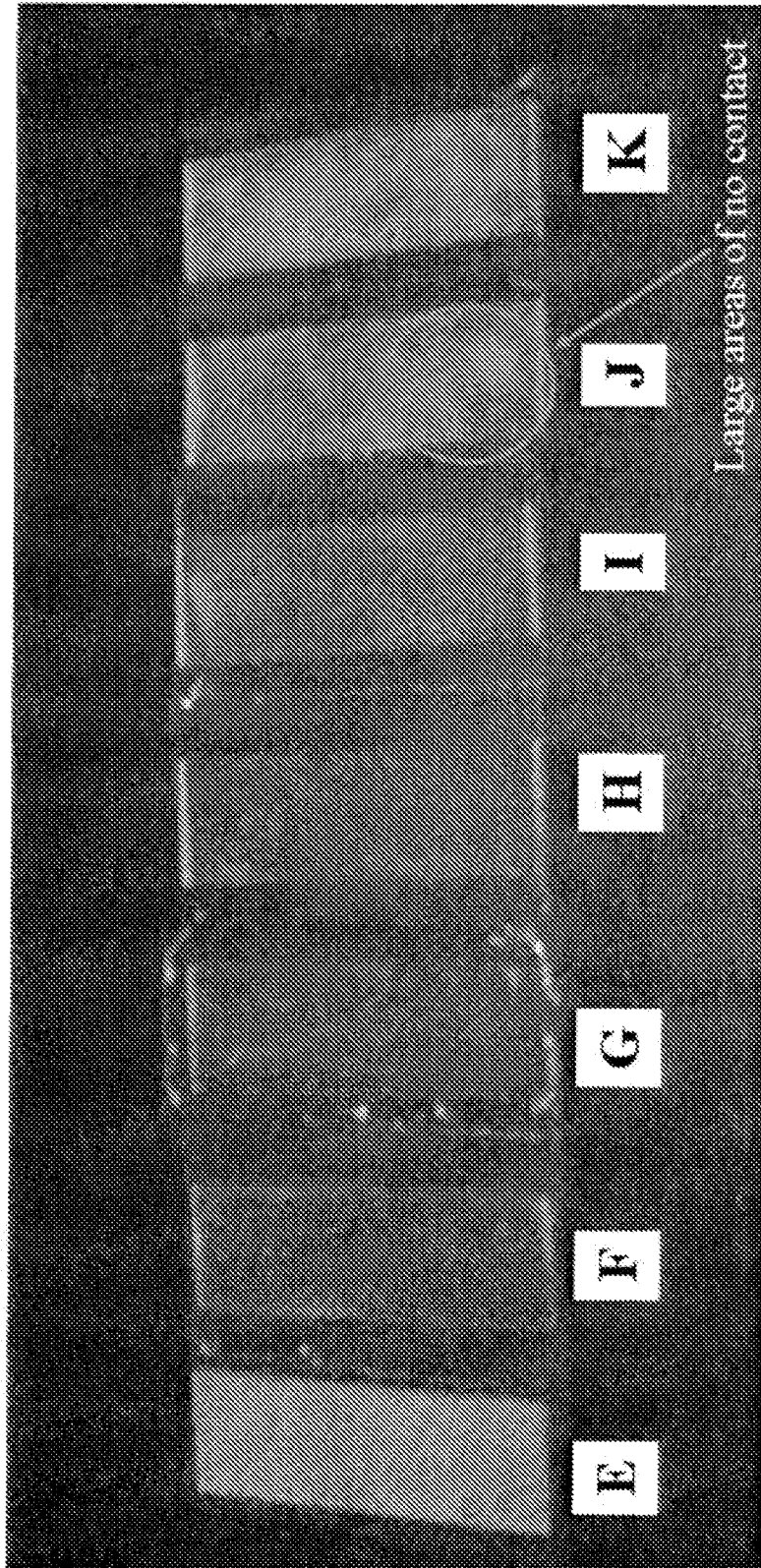
## EXHIBIT B

Set #1 Sample Comparison -- Crossover Zone



The cross-over temperature is defined as the temperature at which the Loss modulus (liquid like behavior) becomes dominant over Storage modulus (elastic behavior)

## EXHIBIT C



## EXHIBIT D

Example	Mw (g/mol)	Normalized Max Peel Strength
L	35,000	0.6
M	50,000	1
N	55,000	1.5
O	68,000	1.7
P	90,000	0.6

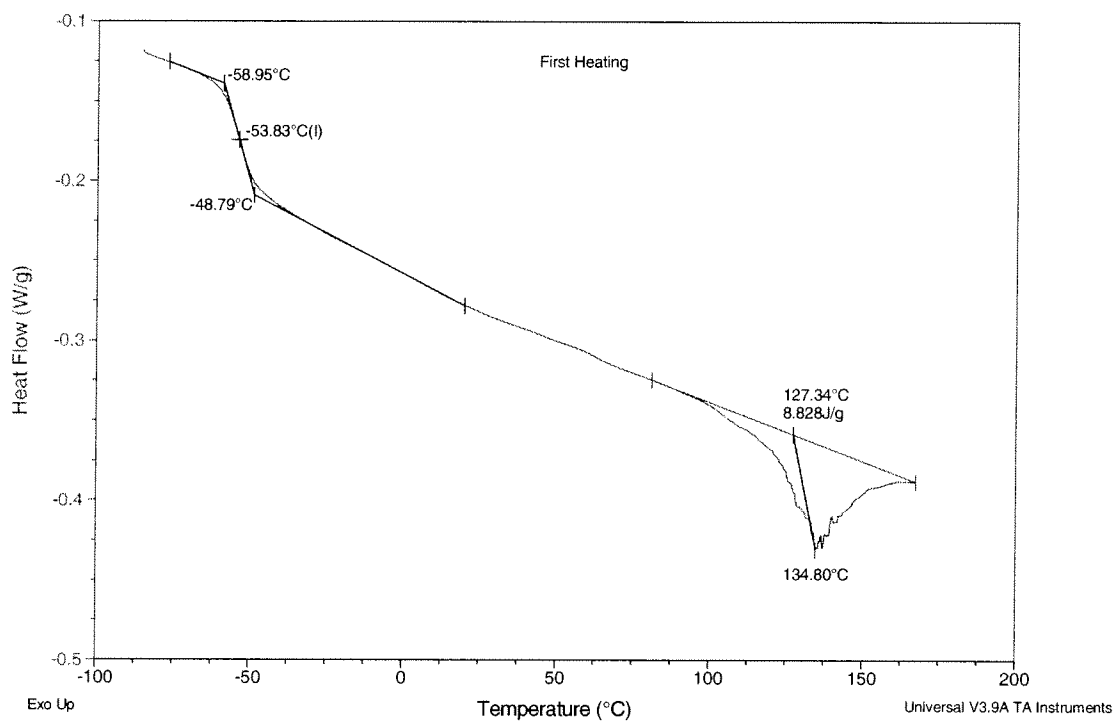
## EXHIBIT E

## Example Q

Sample: 19258-84A  
Size: 10.7920 mg  
Method:  $\beta=10$ , -90 to 170, HCH  
Comment:  $\beta=10$ , -90-170, cool, repeat

DSC

File: E:\Data\Q1000 DSC\SF82686.001  
Operator: TLS  
Run Date: 23-Aug-04 17:33  
Instrument: DSC Q1000 V8.1 Build 261



## EXHIBIT E (Continued)

## Example R

Sample: 19258-89A  
Size: 11.4860 mg  
Method:  $\beta=10$ , -90 to 170, HCH  
Comment:  $\beta=10$ , -90-170, cool, repeat

DSC

File: E:\Data\Q1000 DSC\SF82686.003  
Operator: TLS  
Run Date: 23-Aug-04 20:40  
Instrument: DSC Q1000 V8.1 Build 261

